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The Isolation of Organic Compounds Using Organophilic Pervaporation Membranes

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Review Paper

The Isolation of Organic Compounds using Organophilic Pervaporation Membranes

Brian Bolto *, Zongli Xie, Manh Hoang

CSIRO Manufacturing, Private Bag 10, Clayton South MDC, Victoria 3169, Australia

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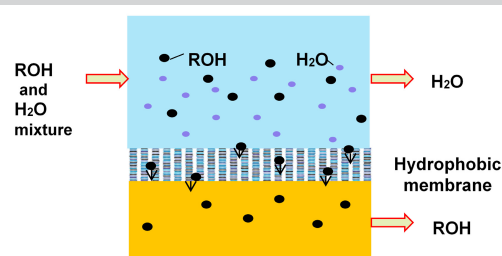
Highlights

- Organophilic membranes can selectively recover organic compounds by pervaporation
- Non-polar structures preferred, whether organic, inorganic, or a mixture of same
- For ethanol recovery, a thin supported layer of silicone rubber gives highest flux rates
- For butanol recovery, flux rates best for silicalite on alumina support
- Metal-organic frameworks have great potential in the separation of organic isomers

Abstract

Organophilic membranes provide a method of recovering organic compounds by pervaporation, which exploits the selective transport of the organic phase. The main application is in the extraction of bio-alcohols from aqueous solution. The effect of membrane composition on performance in transporting alcohols and not water at improved rates is the focus of this review. In this way the minor fraction, the bio-fuel, is removed rather than the usually large volume of water. A more economical process is then obtained. The most successful membranes are non-polar in character, and can be purely organic, inorganic or organic-inorganic polymer hybrids. For ethanol recovery, flux rates are best for polydimethylsiloxane (PDMS) when used as a very thin layer on a supporting base. Zeolites give the best separation factors along with reasonable fluxes, and supported silicalite performs well. For butanol recovery, flux rates are best for PDMS mixed matrix membranes. A styrene copolymer membrane gives a reasonable result for benzene/cyclohexane separation, while metal-organic frameworks have potential in the separation of organic isomers, where pore geometry becomes important.

Graphical abstract



Highest flux membranes

For ethanol recovery: polydimethylsiloxane on a ceramic membrane.
 For butanols recovery: silicalite on an alumina membrane,
 zinc(2-methylimidazolate)₂ on polymethylphenylsiloxane.
 For organics separation: styrene SBR membrane for *n*-hexane/benzene,
 Metal organic frameworks for xylene isomers.

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* Corresponding author at: +61395452037; fax: +61395452037
 E-mail address: brian.bolto@csiro.au (B. Bolto)

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1. Introduction

The isolation of alcohol from fermentation liquors is best carried out by a method that allows removal of this minor component rather than the removal of the water phase, as occurs with hydrophilic pervaporation (PV). PV provides a general method for separating volatile mixtures of liquids. It can be used to remove water as in desalination or the dehydration of aqueous solutions of organic compounds. It is also used in the reverse system of removing organic compounds from aqueous solution, and in the separation of non-aqueous compounds and even their isomers. Ethanol dehydration is the most advanced of the PV processes, and commercial systems have been developed since the 1980s, mostly because of interest in the pharmaceutical industry and the production of pure ethanol as an alternative liquid fuel, where the process can be used to dehydrate azeotropic ethanol/water mixtures [1]. The 200- to 500-fold separation achieved is due entirely to the selectivity of the membranes used, which are much more permeable to water than to ethanol. More than 100 plants for the dehydration of ethanol have been installed, the largest processing 5,000 kg/h.

In continuous fermentation it is essential to remove alcohol before its cell toxicity level is reached. Membranes for the recovery of ethanol have been reviewed [2-5]. There are more than 240 articles in the general area of ethanol recovery [6,7], but usually involving dehydration via hydrophilic PV. In contrast, more hydrophobic membranes allow the design of systems that permeate alcohols more readily than water. This has been reviewed extensively for biobutanol production [8] and for the removal of many other organic compounds from aqueous solutions [9-11]. The effect of membrane composition on organophilic pervaporation (OPV) performance is the main focus of this review. The general principle of OPV is shown in Figure 1.

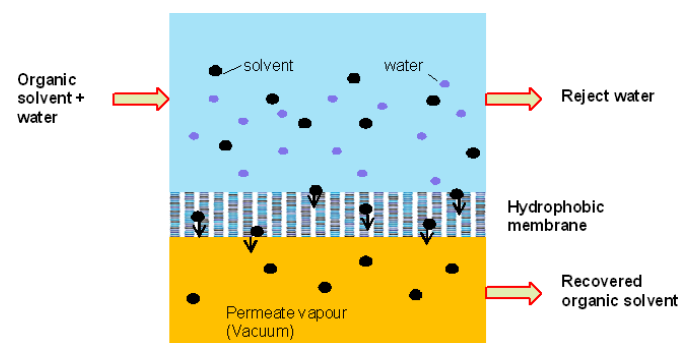


Fig. 1. Operation of the OPV process.

A unique feature is the ability of the membrane to retain the smaller water species (0.28 nm), but allow the permeation of larger organics (≥ 0.38 nm). There is a push to develop more selective membranes for OPV, as well as for membrane bioreactors, bioethanol upgrading, and reactive and membrane-assisted distillation, which are areas that have received little attention [12,13].

The results are often expressed as the total flux J through the membrane and the separation factor α_{sep} [14].

$$J = \frac{W}{At} \quad (1)$$

where W is the weight of permeate collected, A is the effective area of the membrane exposed to the feed, and t is the time that permeate was collected in the trap.

The separation factor α_{sep} can be defined for a two-component liquid system as the ratio of the two components on the permeate side divided by the ratio of the two components on the feed side of the membrane. This can be expressed via the concentration, mole fraction or vapour pressure of the components. For example, the separation factor for an aqueous ethanol solution could be defined as:

$$\alpha_{sep} = \frac{P_{EtOH}/P_{H_2O}}{F_{EtOH}/F_{H_2O}} \quad (2)$$

where P_{H_2O} and P_{EtOH} are the mass or mole fractions of water and ethanol in the permeate, and F_{H_2O} and F_{EtOH} are the mass fractions of water and ethanol in the feed [15].

Mass transport modelling of ethanol removal from aqueous solutions has shown that the feed flow rate has no significant effect on either flux or selectivity, whereas the feed concentration, temperature and permeate-side pressure have highly significant effect [16].

In water treatment it is well established that hydrophobic surfaces of all types encourage the binding of organic compounds, common knowledge in water treatment processes [17]. The opposite system of high hydrophilicity and charge show the opposite effect, as shown in a reviews of nearly 200 examples of modification with hydrophilic entities and about 20 examples of charge modification in membranes used for water treatment [18-20].

2. Polysiloxane membranes

The prime candidates are hydrophobic rubbers like polydimethylsiloxane (PDMS) and poly(trimethylsilyl-1-propyne) (PTMSP), although glassy

amorphous polymers such as polyacetylene, poly(4-methyl-2-pentyne) or PAPMP have received attention also. The general properties of silicone rubber composites have been reviewed [21].

2.1. Polydimethylsiloxanes

The chemical structure of PDMS is:



The results from studies of butanol recovery by OPV using membranes based on PDMS have been summarised [8]. To enhance performance, use has been made of a range of supporting membranes, from cellulose acetate and polyamide to polystyrene and fluorinated polymers [6]. Also, much work has been done on PDMS block or graft copolymers and blends [22].

2.1.1. Supported membranes

One example of PDMS inside a porous poly(vinylidene fluoride) (PVDF) membrane had a flux of 0.0015 kg/m²h and a separation factor of 14 [23]. PDMS has been deposited onto the surface of tubular ZrO₂/Al₂O₃ porous ceramic supports, to give a 5–10 µm thick layer. A total flux of 20 kg/m²h and selectivity of 6 was found for ethanol for a 4.3 wt % aqueous solution at 70°C [24]. Another example of depositing a dense thin-skinned layer of crosslinked PDMS onto a ZrO₂/Al₂O₃ ceramic supporting membrane gave a flux of 13.0 kg/m²h for ethanol removal from a 4.2 wt% solution at 60°C [25]. A pressure of 500 Pa was applied, and a separation factor of 8.3 determined. Similar PDMS composite membranes supported on ceramic hollow fibres have been tested for recovery of *n*-butanol from aqueous solution, with fluxes ranging from 0.46 to 1.28 kg/m²h at 40°C [8,26,27]. An application example of this type of membrane is in the direct recovery of alcohols from a sugar beet fermenter, by recycling the contents of the fermentation broth through a membrane module. This retains cell viability and makes it possible to completely convert sugar in a shorter fermentation time [28]. The performances of such polymer/ceramic composite membranes have been reviewed [29].

PDMS has been formed as an active skin layer on a polysulphone or polyamide supporting layer show for the latter a flux of 1.8 kg/m²h and a separation factor of 8.5 for a 4 wt.% ethanol solution at 45°C [30]. Coatings of PDMS on PVDF have produced a membrane onto which polyphenylsiloxane (PPhS) has been deposited [31]. The composite membrane was tested in the separation of butanol from an acetone/butanol/ethanol (ABE) fermentation liquor. The butanol flux of the PPhS/PDMS/PVDF membrane was 0.33 kg/m²h for a 3 wt.% feed at 30°C, which was higher than that of the PDMS/PVDF membrane. A later effort used a PDMS composite membrane on a PVDF microfiltration (MF) membrane as a support [32]. One with a 6 µm layer gave a separation factor of 4 and a total flux of 0.5 kg/m²h in the separation of dimethyl carbonate from methanol at 40°C.

A crosslinked PDMS/brominated polyphenylene oxide copolymer has been made on a ceramic tube [33]. In the recovery of butanol the flux was 0.22 kg/m²h at 40°C, or about half that of the corresponding PDMS membrane. The separation factor was 35 versus 23 for the latter. However there was much more stable OPV performance.

The performance of a commercial hydrophobic NF membrane, SolSep 3360 from Apeldoorn, the Netherlands, for the removal of ethanol from aqueous solutions by organophilic PV has been described [34]. The membrane had a PDMS top layer. It was compared with a traditional dense PDMS membrane, PV 1070 made by Sulzer Chemtech Ltd. for OPV purposes. For the NF membrane the flux range was 0–3.5 kg/m²h, versus <0.3 kg/m²h for the organophilic membrane, while the separation factor was comparable. For a 20.4 wt.% ethanol/water solution at 44°C it had a flux of 2.1 kg/m²h. The results were ascribed to the larger free volume of the NF membrane and to the stronger interaction between the ethanol molecules and membrane surface. There was a greater swelling of the membrane too.

A membrane with PDMS on a PAN support has been made and its behaviour explored for the removal of product from solutions modelling ABE fermentation [35]. At a feed temperature of 42°C the fluxes were in the order of acetone > butanol > ethanol with values of 0.90, 0.75 and 0.23 kg/m²h respectively for a 3 wt.% component content. The separation factors were 21–26, 22–29 and 5–7. Permeation of butanol seemed to be preferable in solutions of several organic compounds. It was felt that the membrane had potential for use in the ABE fermentation process. The pervaporative recovery of ABE during continuous cultivation has been explored with a PDMS membrane,

with an average flux of 0.62 kg/m²h being obtained [36].

2.1.2. Copolymers and blends

Polystyrene/divinylbenzene interpenetrating networks with PDMS have been prepared which exhibit ethanol selectivity regardless of the extent of PDMS content [22,37]. This was discussed from the point of view of their microphase-separated structures. All the membranes had structures in which polystyrene domains existed in a continuous PDMS phase. Membranes with a PDMS content >40 wt.% had an ethanol permselectivity the same as that of the PDMS membrane. Ethanol preferred to diffuse through the continuous PDMS phase than through the polystyrene phase.

A blend of PDMS with copoly(*N*-isopropylacrylamide/ 1H,1H,2H,2H-perfluorododecyl acrylate) showed a higher separation factor of 20 [38]. A novel polysilicone that contained PDMS and ladder-like phenylsilsesquioxane segments had a reasonable separation factor at low ethanol concentrations [37]. Other examples include a graft of poly(vinylidene fluoride), or PVDF, onto PDMS, and a similar graft of poly(1-phenyl-1-propyne), plus modification of a PDMS membrane with hexamethyldisiloxane. All showed a preference for ethanol over water, but with separation factors below 10. Further low separation factor systems have been evaluated [6].

Segmented PDMS/imide copolymers have been synthesised from α,ω-(bisaminopropyl) dimethylsiloxane oligomers and aromatic dianhydrides such as 1,2,4,5-benzenetetracarboxylic dianhydride and 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-bis-1,3-isobenzeneurandione to produce a high content of siloxane blocks of up to 94 wt.% [39]. Treatment of 10 wt.% ethanol was achieved with a flux of 0.56 kg/m²h and a separation factor of 10.6 at 40°C.

A PDMS blend with a polymer made from ethylene propylene diene forms a composite membrane in which the two components have a rubbery chain structure [40]. The membrane was used in a continuous membrane bioreactor and compared with results obtained with a batch fermenter. Ethanol production from molasses was found to be higher in the continuous version than that from the batch system operated for 24 h.

A poly(styrene-*b*-dimethylsiloxane-*b*-styrene) membrane has been tested for *in situ* product recovery during fermentation, to enable the development of a continuous fermentation process [41]. The styrene blocks enhanced the robustness of the membrane, and the OPV performance was comparable with that of PDMS membranes.

2.1.3. PDMS analogues

A variation is the use of poly-octylmethylsiloxane (POMS) on a polyacrylonitrile (PAN) support for ethanol recovery from aqueous solution [42], and for similar bio-butanol removal [43]. Reasonable selectivities were found for the alcohols but low fluxes. For 1.5 wt.% bio-butanol the flux was 0.28 kg/m²h, with a selectivity of 42. A similar POMS/PAN membrane was tested on a 10 wt.% ethanol/water mixture at 63°C and had a flux of 0.95 kg/m²h [44].

Poly-phenylmethylsiloxane (PPhMS) deposited on a cellulose acetate MF membrane resulted in fluxes of 1.43 kg/m²h in the separation of ethanol from 5 wt.% solutions at 40°C, versus 1.14 kg/m²h for the corresponding PDMS membrane [45]. The separation factors were 6.2 and 9.3 respectively. The PPhMS species was more hydrophobic than the PDMS type, and was also better for removing methanol and acetone from aqueous solution.

A PDMS membrane with pendant phenoxy groups that was deposited on a porous PVDF support has given good performance with a flux of 2.85 kg/m²h and a separation factor of 4.6 for a feed of 10 wt.% ethanol at 30°C [46].

2.1.4. Commercial PDMS membranes

Commercial PDMS membranes used for OPV such as Pervap 1060, 2200 and 4060, made by Sulzer Chemtech Ltd., Switzerland, and those from PolyAn GmbH, Berlin, have been employed in the OPV removal of acetone, butanol and ethanol (ABE) from binary aqueous solutions [8], where the membranes are selective for butanol. An organophilic PV/hydrophilic PV process has been employed to separate and purify *iso*-butanol from its dilute aqueous solutions [47]. A composite PDMS membrane supplied by Helmholtz-Zentrum Geesthacht Zentrum für Material und Küstenforschung GmbH, Geesthacht, Germany was used to isolate the *iso*-butanol and a poly(vinyl alcohol) or PVA membrane, Pervap 2210, has been used to dehydrate it. Earlier work had shown that PDMS membranes are more permeable to *n*-butanol than *t*-butanol, and that they are more effective than a polymethoxysiloxane membrane, as measured by both selectivity and flux [48]. For a PDMS membrane operating with a 130 Pa permeate side pressure the respective fluxes were 1.0 and 0.5 kg/m²h at 50°C, and the selectivities 33 and 20, contrary to the usual observation that faster membranes are less selective.

Other companies manufacturing PDMS membranes include SolSep BV,

Netherlands and the Celanese Corporation, the USA [6]. Fluxes of current unmodified PDMS membranes can vary from 0.001 to 1 kg/m²h, with separation factors of less than 10 [49]. This is ascribed to their rubbery mechanical properties and high swelling behaviour.

2.1.5. Poly(trimethylsilyl-1-propyne) (PTMSP)

Poly(trimethylsilyl-1-propyne) or PTMSP is a dense rubbery polymer that yields separation factors ranging from 9 to 26 times higher than those of PDMS [50]. The structure is:



It has definite advantages over PDMS, a silica filled polytetrafluoroethylene (PTFE) membrane with a PTMSP layer of 2.4 μm thickness, in that it has a flux of 9.5 kg/m²h and a separation factor of 104 for butanol recovery at 50°C [51], versus a flux of 1 kg/m²h and a separation factor of 33 at 50°C for PDMS [48]. The higher separation factor for PTMSP most likely arises from the less polar nature of that membrane, which would adsorb butanol more strongly onto its active surface.

It is unfortunate that PTMSP ages physically or chemically so that its performance deteriorates with time [48]. Modifications have been made to avoid deterioration of PTMSP by using different catalysts in its preparation, and by grafting other polymers on to it such as PDMS and polymers containing alkylsilyl groups or fluoroalkyl groups [6]. Another approach makes use of blending in a graft copolymer made from polyfluoroacrylate and PDMS [52], which maintains the enhanced performance.

Fouling of a PTMSP membrane by material from fermentation broths, such as butyric acid and long chain fatty acids, has been shown to be responsible for a fall off in performance. Prior treatment using polyamide nanofiltration (NF) membranes led to a marked improvement in flux and in the butanol-water separation factor, which at 27.5 was higher than the 14.7 obtained with a commercial PDMS membrane [53]. The performance in treating fermentation liquors is less efficient than that reported above for simple solutions, as significant fouling occurs. This is in line with the greater hydrophobic character of the PTMSP membrane [20].

The authors point out that butanols hold tremendous promise as bio-fuels since they combine a considerably higher combustion value than ethanol, with chemical properties that allow straightforward blending with fossil-based fuels. It is also an important commodity chemical as a solvent and as a precursor for chemical synthesis.

2.2. Summary of results for silane membranes

Results for the better performers of membranes based on silane are shown in Table 1. Flux rates are highest for PDMS used as a very thin membrane on a supporting base, with ethanol fluxes of 5.2 to 20 kg/m²h at 40 to 70°C [24], and separation factors of 8.3 and 6 respectively. For butanol recovery the fluxes are much lower, with a PTMSP layer on a PTFE/silica composite membrane being the best, at 9.5 kg/m²h at 55°C, but with a much higher separation factor of 104 [51]. This is a reflection of the less polar structure of PTMSP compared to PDMS.

3. Organic membranes

Hydrophobic membrane materials other than PDMS and its analogues have been explored, as has been reviewed extensively [55], with polypropylene (PP) being effective for benzene/cyclohexane separation. Polytetrafluoroethylene (PTFE) and PP products passed a large amount of water through the membrane [56].

The most notable hydrophobic membranes were made from a 85/15 wt.% mix of styrene and a styrene-butadiene-styrene three block copolymer, prepared in the presence of a hydrophilic polymer such as that from dimethylacrylamide, which give a high flux of 1.04 kg/m²h and a separation factor of 25 in treating 70/30 wt.% benzene/cyclohexane at 20°C [57]. For ethanol, polymers such as nitrile-butadiene rubber, styrene-butadiene, and polysubstituted acetylenes have been investigated [58].

A commercial poly(ether-block-amide) or PEBA membrane, made from nylon 12 and poly(ethylene oxide) blocks and known as PEBAX 2533, has been tested for the separation of binary ethanol/water, acetone/water, and *n*-butanol/water mixtures [59]. The membrane selectivity was found to be in the order *n*-butanol > acetone > ethanol. The very small flux decreased with

increase in the membrane thickness, for 5 wt.% ethanol at 23°C, from 0.013 kg/m²h for a 30 μm thickness to 0.004 kg/m²h for one 100 μm thick. For 5 wt.% *n*-butanol it was 0.04 kg/m²h for the thinner membrane. The paper also reviews the range of other membrane types that have been investigated, but performance is generally not impressive. They include ethylene-propylenediene rubber, styrene butadiene rubber, PP and PTFE.

Table 1

Best OPV performance data for ethanol or butanol recovery from aqueous solution with silane membranes.

Feed (wt.%)	Membrane	Sepr. Factor	Flux (kg/m ² h)	Temp. (°C)	Ref.
Ethanol					
4.3	PDMS 5–10 μm layer/ceramic support	6	20	70	[24]
		6	5.2	40	
4.2	PDMS/ceramic membrane	8.3	13.0	60	[25]
10	Pervatech, 2 μm active layer	6	3.3	50	[51]
10	PDMS/UF membrane	7	4	80	[54]
20	PDMS/NF membrane	-	2.1	44	[34]
4	PDMS/polyamide membrane	8.5	1.8	45	[30]
1.5	PDMS/PTFE membrane	14	1.5	66	[23]
10	Phenoxy PDMS	4.6	2.9	30	[46]
10	PDMS/imide copolymer	11	0.56	40	[39]
5	PTMSP*	-	1.5	60	[48]
			7.6	90	
5	PPhMS†	6.2	1.4	40	[45]
10	POMS** on PAN	-	0.95	63	[44]
Butanol					
<i>n</i> -, 7	PDMS	33	1.0	50	[48]
<i>t</i> -, 7	PDMS	20	0.5	50	
<i>n</i> -, 1	PDMS/ceramic	43	1.3	40	[26]
ABE, 3	PPhS‡ on PDMS/PVDF	3	0.33	30	[31]
Bio-, 1	POMS** on PAN	42	0.28	55	[43]
<i>n</i> -, 5	PTMSP* on PTFE/silica	104	9.5	50	[51]

*Poly(trimethylsilyl-1-propyne);

†Polyphenylmethylsiloxane;

‡Polyphenylsiloxane;

**Polyoctylmethylsilane

Crosslinked and linear *cis*-polybutadiene membranes have been made and tested for the separation of aqueous lower alcohol solutions [60]. They permeated the alcohols in preference to water. For 30 wt.% solutions the selectivity for ethanol was about 10 times greater for the crosslinked version, but the flux was surprisingly doubled for the crosslinked membranes, although quite low at 0.002 kg/m²h.

Fluorinated siloxane-imide block copolymers have been made and tested for removal of trichloroethylene from water by OPV [61]. The membranes were made from moieties containing -CF₃ groups, which enhanced their hydrophobic character. Fluxes of 0.25–0.28 kg/m²h and separation factors of 2600–3300 were observed for 500 mg/L concentrations at 25°C. A novel polysiloxaneimide/polyetherimide composite membrane has been made from 3,3,4,4-biphenyltetracarboxylic dianhydride and an amino-modified siloxane, dual end type [47,62]. The support was a non-woven fabric covered by the porous crosslinked polyetherimide. In the recovery of ethanol from a 5 wt.% aqueous solution at 60 °C the separation factor was ~3 and the flux ~ 0.5 kg/m²h.

A hydroxyl-terminated polybutadiene-based polyurethane urea membrane has been tested for *n*-butanol recovery [63]. For a 2.6 wt.% solution at 40°C the flux was 0.025 kg/m²h and the separation factor 24. A hyperbranched polyether has been vinyl modified by reaction with potassium metal and allyl glycidyl ether. The resultant compound was then used to crosslink the urea membrane. For the recovery of *n*-butanol from a 3.4 wt.% solution at 70°C the crosslinked membrane gave a flux of 0.32 kg/m²h and a separation factor 10 [60,64].

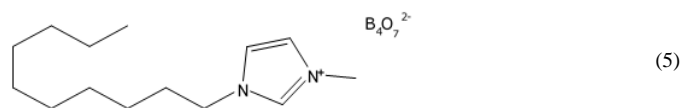
A completely different approach has been the preparation of polymeric

membranes having hydrophobic brush-like structures as a selective layer, by photo-grafting hydrophobic vinyl compounds such as stearyl methacrylate onto PES NF membranes [65]. They have been tested for isobutanol recovery from water, and found to have a higher selectivity than a PDMS membrane for a 6 vol.% solution, at 10.1 versus 6.7, with a similar flux behaviour of ~0.6 kg/m²h (no temperature cited).

4. Supported ionic liquid membranes

Supported ionic liquid based membranes are formed from very hydrophobic and bulky organic cations (such as *N*-alkylpyridinium or 1-alkyl-3-methylimidazolium) and inorganic or organic anions, with the liquid being encased in a supporting material. They have attracted much attention because of their possible structural variations, including polar characteristics, and their good selectivity and usefulness in a number of applications such as catalysis, extraction and resolution [66]. Details of several examples of the latter have been published, including biogas upgrading [67].

A porous nylon or PP supporting membranes have been tested for *n*-butanol recovery [68]. The ionic component in the best product was 1-decyl-3-methylimidazolium tetraborate:



OPV at 37°C on aqueous *n*-butanol of 5 wt.% organics achieved a flux of 0.56 kg/m²h to give a permeate of 55 wt.% concentration. However, leakage of the ionic liquid was noticeable. A solution to this would be to covalently bond the ionic component to the support, as has been suggested following an adsorption study on 1-butyl-3-methylimidazolium and its (trifluoromethylsulfonyl)imide and hexafluorophosphate salts [69]. The first of these gave the better adsorption and selectivity results for *n*-butanol, showing a great affinity for butanol and a reasonable rejection of water. An ionic liquid in the form of 1-methylimidazolium *bis*-trifluoromethylsulfonylimide has been covalently bound to a PDMS backbone polymer [70]. In the recovery of ABE from fermentation broth, the flux at 0.16 kg/m²h was 7.8 times greater than that of the conventionally supported ionic liquid-PDMS membrane, where attachment was by physical adsorption onto the supporting membrane, and there was thrice the butanol enrichment. In addition, there better long-term operational stability. Although the flux was only 13% greater than that of the parent PDMS membrane, there was 3.5 times the enrichment factor.

A further similar membrane has been made by the gelation of an ionic liquid, composed of

1-butyl-3-methylimidazolium hexafluorophosphate, into the pores of PTFE hollow fibres [71]. In OPV of ABE liquors there was improved butanol/ethanol selectivity compared to that of the empty PTFE fibres. The results were moderately lower than those for an equivalent filled membrane using a non-gelled ionic liquid.

OPV has proved to be one of the best methods for removing organic compounds from a *Clostridium acetobutylicum* culture. By using a UF membrane (pore size 60 nm) impregnated with 15 wt.% of (tetrapropylammonium tetracyano-borate) and 85 wt.% of PDMS, it was observed that there was high selectivity at 37°C, with a flux of 0.14 kg/m²h at 37°C. There was stable and efficient removal of *n*-butanol and acetone [72].

Another gel-based ionic liquid membrane has been formed from tetrahexyl(tetradecyl) phosphonium dicyanamide and poly(vinylidene fluoride-co-hexafluoropropylene), coated onto porous PP [73]. In treatment of dilute *n*-butanol solution the gelling significantly improved the operational life to 80 h, compared with 10 h for the non-gelled product. The butanol flux was about 0.15 kg/m²h for a 1 wt.% solution at 40°C. So far, fluxes are not impressive. As well, something more substantial than gelling needs to be done to prevent leakage. One possibility is to use polymeric forms of the ions, linking them via poly-salt formation into a quite insoluble species.

The ionic liquid membranes have been prepared by immobilising the ionic liquids 1-hexyl-3-methylimidazolium hexafluorophosphate or 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide within a PDMS membrane, following by hardening with PDMS by poly-condensation [74]. In general, the parent PDMS membrane offered high butanol flux but low selectivity. In contrast, the ionic liquid/PDMS membranes had a high affinity for butanol and showed a higher butanol selectivity, but had a low flux. The flux for the best of them with the more hydrophobic imide salt was 0.94 kg/m²h for a 3 wt % solution at 50°C. This membrane also had the highest selectivity.

Trioctylamine has been explored as a liquid membrane for removing

solvents from fermentation broths [3]. The amine was immobilised in the pores of a PP hollow fibre membrane that had a nanoporous fluorosilicone coating on the outside of the fibres. This was purported to prevent contamination from loss of amine to the feed solution. The selectivities for butanol, acetone and ethanol for 1.5/0.8/0.5 wt.% content of each in a quaternary aqueous solution at 54°C were 275, 220 and 80, with fluxes of 0.011, 0.005 and 0.0012 kg/m²h respectively. The fluxes could be increased by a factor of 5 by reducing the thickness of the amine layer in the porous wall of the coated fibres. Stability with no loss of amine was claimed for 300 h of operation, but it is difficult to accept that leach out would not occur in the long term. Also, the membrane is pH sensitive and fully protonated at low pH.

5. Inorganic membranes

5.1. Zeolite membranes

Zeolite membranes have been prepared by depositing polycrystalline layers on porous supports. They have both good flux and superior selectivity behaviour, and have low swelling and high thermal and chemical resistance [4]. Their use in OPV was reviewed some time ago, where it was emphasized that their main application so far has been for hydrophilic versions in dehydration processes [75]. All-silica zeolites are more chemically and thermally stable than aluminium-containing zeolites.

A NaA zeolite membrane has been demonstrated to have, for a 10 wt.% ethanol solution, a flux of 4.5 kg/m²h and a separation factor of 30,000 at 105°C. At 75°C the results were 2.2 kg/m²h and 10,000 respectively [76].

MFI-zeolite membranes supported on ceramic capillaries have been prepared with microwave heating in order to reduce the preparation time so that dissolution of the support did not occur [77]. The zeolite layer was deposited both inside and outside the capillaries.

In the treatment of 5 wt.% ethanol/water at 45°C a flux of 1.5 kg/m²h and a selectivity of 54 were obtained. Similar MFI-zeolite membranes have been deposited on an alumina support and evaluated for separation of 3 wt.% *n*-butanol/water and 10 wt.% ethanol/water [78]. They were selective for *n*-butanol and ethanol. For the best membrane the *n*-butanol flux was 4 kg/m²h and the separation factor was 10 at 60 °C.

Zeolite membranes deposited on tubular α -alumina supports had fluxes of 0.2 and 1.9 kg/m²h and separation factors of 43 and 25 for 5 wt.% ethanol/water at 25 and 85°C respectively [79]. At low temperatures ethanol blocked water permeation more effectively because of its strong adsorption. The water flux increased more than the ethanol flux with increasing temperature because of a lower coverage of ethanol in the zeolite pores, resulting in lower separation factors at higher temperatures. Zeolites have the advantage that the hydrophilic/hydrophobic balance can be modified by introducing different metals into the framework and by changing the Si to metal ratio [80]. Thus elements such as Al, Fe, B and Ge have been substituted into silicalite and ZSM-5 zeolite structures to give ethanol separation factors in the sequence Ge > Al > Fe > B, with values ranging from 29 to 2.1, but fluxes of only 0.1 kg/m²h or lower. This indicated that Ge produced the most hydrophobic membrane, a fact that was confirmed by absorption tests.

MFI zeolite membranes have been de-templated by calcination and ozonation [81]. One membrane was calcined at 500°C, and the other ozonated at 200°C. The separation factors of both membranes were similar and ranged from ~20 at 100°C to ~40 at 75°C. The calcined membrane showed an 80% higher flux than the ozonated membrane, indicating that ozonation could not completely remove the template. The incomplete de-templation was attributed to the presence of aluminium in the zeolite layer which was leached from the support layer and incorporated into the zeolite structure during synthesis. Using ozone allowed the de-templation of zeolites to be carried out at temperatures far below conventional calcination temperatures. Because the zeolite was not heated above 200°C, the silanol groups in the zeolite framework were preserved. Of some 18 other similar membranes the fluxes obtained were all below 1 kg/m²h [6].

The separation of organic/water mixtures with a mesoporous MCM-48 silica membrane silylated with trimethylchlorosilane to enhance hydrothermal stability and hydrophobicity has been reported [82]. The membranes were made on a porous alumina support, and used in tests of the separation of ethyl acetate, methyl ethyl ketone and ethanol from water. The separation factors and fluxes were in that order. The flux and separation factor for ethanol were the lowest, at 0.14 kg/m²h and 11 for 10 wt.% ethanol/water at 30°C. For a non-silylated membrane the results were 0.12 kg/m²h and 0.6 respectively. With the silylated membrane the pore blocking effect due to the selective adsorption of the organic molecules caused a greater obstruction to the diffusion of water molecules through the membrane pores. It was thought that

the high selectivity was attributable to not only the hydrophobic nature of the pore surface, but also to the uniform mesopores of the membranes, which were estimated to be 1.9 nm in size.

5.2. Silicalite membranes

In early work, organic/water mixtures were separated by OPV through silicalite, a hydrophobic polymorph of SiO_2 that has a structure analogous to the zeolites. Methanol, ethanol and acetone are preferentially removed before water from aqueous solution [83]. The transport mechanisms of ethanol/water mixtures by OPV and vapour permeation through a silicalite membrane have been investigated [84]. Ethanol transport was found to be independent of the water concentration in the feed; water permeation was seriously affected by the presence of ethanol.

Silicalite membranes supported on macroporous $\alpha\text{-Al}_2\text{O}_3$ tubes have been made by the use of ethyltriethoxysilane as the silica source [85]. A flux of 1.5 $\text{kg/m}^2\text{h}$ was obtained for 5 wt.% ethanol at 60°C, together with a separation factor of 39. For 2 wt.% butanol the results were 0.10 $\text{kg/m}^2\text{h}$ and 150. The pore size of the silicalite was evidently too small to allow easy passage of the higher alcohol. A similar study of silicalite particles deposited onto $\alpha\text{-Al}_2\text{O}_3$ but by simply seeding with a water slurry of silicalite particles followed by hydrothermal treatment gave a membrane with a flux of 1.8 $\text{kg/m}^2\text{h}$ for 5 wt.% ethanol at 60°C, with a higher separation factor of 89 [86]. Another method for preparing silicalite membranes involves hydrothermal synthesis onto tubular supports [87]. Fluxes were up to 4.0 $\text{kg/m}^2\text{h}$ for 10 wt.% ethanol at 60°C, with a separation factor of 30.

A capillary titanosilicalite has been made by microwave assisted heating and trialled for ethanol recovery from a 5 wt.% solution at 65°C [88]. The flux was 2.2 $\text{kg/m}^2\text{h}$ and the separation factor 48.

Inorganic membranes based on silicalite and ZSM-5 zeolite have been the main types that have been explored. Such zeolites contain straight and zig-zag pores with an opening of ~0.55 nm. Membranes have been made from titania and an ZSM-5 zeolite deposited on a multi-layered ceramic supporting membrane [89]. For a feed concentration of 5 wt.% ethanol a permeate concentration of 84 wt.% ethanol was obtained at a flux of up to 1 $\text{kg/m}^2\text{h}$ when the feed temperature was 40°C.

5.3. Summary of results for inorganic membranes

A summary of the best results for inorganic membranes is shown in Table 2. Separation factors are greatest for NaA zeolite, with fluxes of 2.2 to 4.5 $\text{kg/m}^2\text{h}$ for ethanol at 75 and 105°C [76], and for silicalite, which in one form attains a flux of 4 $\text{kg/m}^2\text{h}$ at 60°C [87]. The available commercial membranes are from Membrane Technology and Research, Nanotech, GKSS, Sulzer Chemtech, SolSep BV and Pervatech [5,90,91].

6. Metal-organic frameworks (MOFs)

MOFs are coordination polymers based generally on a ligand L having at least two coordinating groups in a bidentate structure. They are $-\text{L}-\text{M}-\text{L}-\text{M}-$ alternating copolymers, usually in a three-dimensional format with crosslinking via the metal M. MOFs show great potential and versatility for OPV because they offer a wide range of choices in the balance of organophilic and hydrophilic structures within the membranes, consisting as they do of a range of metal ions that are interconnected by an organic ligand. Membranes of this type have been comprehensively reviewed [91–97], with the emphasis on gas separation and a wide range of other applications [98]. More than 20,000 MOF structures have been reported and current efforts in the area are many. There is an ability to vary the size and nature of MOF structures without changing their underlying topology. A porosity of greater than 50% of the MOF volume is achievable, giving surface areas ranging from 1,000 to 10,000 m^2/g , exceeding those of other adsorbents such as zeolites and carbons.

The major advance in the area has been the linking of previously prepared secondary building units with organic ligands, rather than synthesis by simply forming coordination polymers from metal ions and the ligands [95]. This was central in achieving permanent porosity in MOFs and also resulted in the use of the isoreticular principle of varying the size and nature of a structure without changing its underlying topology. It makes possible the design of MOFs with very high porosity and unusually large pore openings. Many building units has been studied, some of which are relevant to OPV and will be briefly mentioned here. Organic structures other than phenyl, such as biphenyl, tetrahydropyrene, pyrene, and terphenyl have been incorporated between metal centres and found to result in pore sizes that vary incrementally from 0.38 to 2.9 nm [99]. MOFs may be used alone as a membrane, added to a suitable support system, or be part of a mixed matrix

arrangement with a host polymer.

Table 2

Best performance data for ethanol and butanol recovery using inorganic membranes.

Feed, (wt.%)	Membrane	Sep. factor	Flux ($\text{kg/m}^2\text{h}$)	Temp. (°C)	Ref.
Ethanol					
10	Silica/trimethyl chlorosilane	11	0.14	30	[82]
5	Silicalite on Al_2O_3	3	1.5	60	[85]
5	Silicalite on steel support	89	1.8	60	[86]
5		30	4.0	60	[87]
5	Titanosilicalite	48	2.2	65	[1]
5	Titania and ZSM-5 zeolite	-	1.0	40	[89]
5	ZSM-5 zeolite on Al_2O_3	43	0.2	25	[79]
5	NaA zeolite	25	1.9	85	[79]
10		-	2.2	75	[76]
		-	4.5	105	
5	MFI zeolite on ceramic capillaries	-	1.5	45	[77]
Butanol					
2	Titanosilicalite	150	0.10	60	[85]
10	Silicalite on Al_2O_3	10	4.0	60	[78]

6.1. Terephthalate frameworks

The first successfully synthesised MOF was made from zinc oxide and terephthalate, and is known as MOF-5. It is a coordination polymer with the terephthalate units linked by zinc ions, and also crosslinked by them. Many structures have been drawn for such species, showing the way that the pore size can be adjusted by changing the organic ligand, which also provides the hydrophobic character of the system [100]. MOF-5 is noted for its large pore size (0.8 nm) and aperture sizes (1.2 and 1.5 nm). The flux for *p*-xylene through a MOF-5 membrane is 0.7 $\text{kg/m}^2\text{h}$ at room temperature, and is half that for the *o*- and *m*- isomers, suggesting that the membrane can be used for separating organic compounds based on molecular sieving effects, with molecules larger than the pore size being excluded [101]. However, MOF-5 undergoes severe degradation on contact with water.

The flux of a PDMS membrane for ethanol recovery has been enhanced by incorporation of MIL-53 particles, made from aluminium chloride and terephthalic acid (TPA), and named after the Materials Institute Lavoisier [102]. The material is remarkable for its breathing properties, in that a volume change of 40 to 230% can be brought about by adsorption or desorption of guest molecules [103]. For ethanol recovery from a 5% aqueous solution at 70°C, compared to an unloaded PDMS membrane the 40 wt.% composite had a flux of 5.5 versus 1.7 $\text{kg/m}^2\text{h}$, while the separation factor remained at 11. The enhancement of flux was attributed to the water repellent surface and ethanol-affinity channels of the MIL-53 particles.

Zinc terephthalate(triethylenediamine)_{0.5} is a very hydrophobic MOF which has interlacing channels. The adsorption and separation of methanol/water and CO_2/CH_4 with this MOF have been investigated experimentally and by simulation, with the results being in fairly good agreement [104]. While water adsorption was quite small, methanol adsorption was much greater. The methanol interacted intensely with the metal oxide centres. The selectivity of methanol versus water was approximately 20 at low pressures, and decreased with increasing pressure. The results suggest that $\text{Zn}(\text{TPA})(\text{TED})_{0.5}$ is a good candidate for the separation of alcohol/water mixtures and alcohol-based liquid fuels.

Zinc terephthalate(1,4-diazabicyclo-2,2,2-octane) or $\text{Zn}_2(\text{TPA})_2\text{DABCO}$ is made by heating a dimethylformamide solution of zinc nitrate, phthalic acid and 1,4-diazabicyclo-2,2,2-octane to give a crystalline product. This was linked to a porous silica substrate that had been modified with 3-aminopropyltriethoxysilane to produce a continuous membrane [105]. The pore size of this type of membrane was 0.75 nm. Separation tests of xylene isomers at different temperatures from 25 to 200°C were carried out, and good fluxes were obtained at high temperature. As the temperature was increased from 25 to 150°C for the *m*-xylene/*p*-xylene binary system, the flux of *m*-xylene increased from 0.83 to 2.1 $\text{kg/m}^2\text{h}$, while for *p*-xylene it only slightly increased from 0.41 to 0.53 $\text{kg/m}^2\text{h}$. However, at 175 to 200°C, the

membrane gradually became unstable. This MOF has been introduced into a PEBA polyether membrane with a 20 wt.% loading to form a mixed matrix membrane that has improved mechanical properties [106]. For a model ABE fermentation broth it exhibited a high total flux of 0.63 kg/m²h and an *n*-butanol separation factor of 17.4 at 40°C. The results suggested a promising future for this type of MOF for bio-butanol recovery.

6.2. Zeolitic imidazolate frameworks (ZIFs)

ZIFs are a type of MOF that is topologically isomorphic with zeolites, because the metal-imidazole-metal angle is similar to the Si-O-Si angle in aluminosilicate zeolites. They exhibit exceptionally high surface areas and pore sizes in the range of micropore (>2 nm) to mesopore (2–50 nm).

6.2.1. Zinc(benzimidazolate)₂ (ZIF-7)

ZIF-7, made from zinc nitrate and benzimidazole, has been encased in crosslinked PDMS to form a membrane which is useful in butanol recovery [107]. Membranes containing 20 wt% ZIF-7 were the optimum. Compared with the parent PDMS membrane, they gave an enhanced flux and separation factor. The better flux was ascribed to an enlarged free volume in the polymer matrix provided by the ZIF-7 nanoparticles, the very hydrophobic pores of which may have contributed to the high separation factor. The flux was 1.7 kg/m²h and the separation factor 66, compared to 1.1 kg/m²h and 51 for a PDMS membrane when separating 1 wt% butanol solution at 60°C. For 5 wt.% butanol the results were 3.5 kg/m²h and 70 respectively. The membranes retained structural stability and integrity during 240 h of continuous operation.

6.2.2. Zinc(2-methylimidazolate)₂ (ZIF-8)

A novel organophilic membrane has been made from zinc(2-methylimidazolate)₂, and is known as ZIF-8 [108]. This MOF exhibits superhydrophobicity and an exceptional adsorption selectivity towards *iso*-butanol. The aperture of ZIF-8 has been estimated as 0.34 nm by single-crystal X-ray diffraction [109], whereas the *iso*-butanol diameter is 0.50 nm, indicating a very flexible rather than a rigid framework structure. ZIF-8 also shows a reversible gate opening effect upon variation of the temperature or pressure. Prepared as a mixed matrix membrane with polymethylphenylsiloxane (PMPS), it has been tested on 1–3 wt.% aqueous solutions of *i*-butanol at 80°C, to give fluxes of 6.4 and 8.6 kg/m²h and separation factors of 35 and 40 respectively. This would mean that for a 1 wt.% solution could give a permeate of ~30 wt% *i*-butanol. It has potential in the OPV recovery of bio-alcohols from fermentation broths, being more effective for butanols recovery, but less so for ethanol.

Similar results have been obtained with a ZIF-8/PDMS hybrid membrane with a 40 wt.% loading of the ZIF-8. The membrane showed excellent performance, with a flux of 4.85 kg/m²h and a separation factor of 82 for 1 wt.% *n*-butanol at 80°C [110].

A molecular simulation study of the adsorption of water and alcohols on hydrophilic and hydrophobic MOFs has indicated that for the hydrophilic version the adsorption decreases in the order water > methanol > ethanol, and the reverse applies for the hydrophobic material [111]. ZIF-8 is chemically and thermally stable, and remarkably resistant to water and organic solvents [112].

ZIF-8-filled PDMS membranes have been explored for the separation of *n*-butanol from aqueous solution [113]. Compared with an unfilled PDMS membrane, the PDMS/ZIF-8 membrane showed a higher *n*-butanol selectivity and permeability, the selectivity for *n*-butanol reaching 7.1 at 30°C when the feed concentration of *n*-butanol was 0.96 wt.%.

The unexpected molecular sieving properties open up new opportunities for ZIF materials for separations that cannot be economically achieved with traditional synthetic zeolite microporous adsorbents [114]. Mixed matrix membranes of the ZIF-8/polybenzimidazole type have been tested for the dehydration of aqueous alcohols [115]. They provide good adsorption properties as an adsorbent for ethanol extraction out of water, but are not regarded as an effective membrane candidate for ethanol removal because of a low initial ethanol uptake, unfavourable diffusion selectivity and competitive water uptakes in the adsorbed ethanol phase [116].

A ZIF-8 membrane on an α -Al₂O₃ support has been used to separate *n*-hexane/benzene and *n*-hexane/mesitylene at room temperature, with a flux of 0.43 kg/m²h for the former being obtained at room temperature [117]. Measurements showed that *n*-hexane and benzene are adsorbed by ZIF-8, but mesitylene is not, corresponding to the trend found in the OPV experiments. The mobile component *n*-hexane is blocked by the less mobile benzene. In contrast, with *n*-hexane/mesitylene molecular sieving takes place and with increasing mesitylene concentration the *n*-hexane flux is increasingly reduced by pore entrance blocking.

6.2.3. Zinc(4,5-dichloroimidazolate)₂ (ZIF-71)

An organophilic membrane has been prepared on a porous zinc oxide substrate by reacting zinc acetate and 4,5-dichloroimidazole [118]. With a 5 wt.% ethanol/water solution it had a flux of 0.32 kg/m²h and a selectivity factor of 6.1 at 25°C. The performance is less than that expected from published adsorption data, although it was obtained on material of higher surface area than previous products [119].

A mixed matrix membrane based on ZIF-71 and PMPS has been prepared [97]. It was tested for OPV separation of bio-alcohols and found to have nearly double the flux of unfilled PMPS membranes, with values for 5 wt.% ethanol at 50°C of 1.4 and 0.8 kg/m²h respectively. For 5% *iso*-butanol the flux reached 1.75 kg/m²h. This was despite the butanol size (0.50 nm) being slightly greater than the aperture size of ZIF-71 (0.48 nm).

A ZIF-71 and PEBA mixed membrane with a 20 wt.% loading showed good separation of *n*-butanol in a real acetone/butanol/ethanol fermentation liquor at 37°C, with a total flux of 0.45 kg/m²h and an *n*-butanol separation factor of 18 [120].

Simulation and Fourier transform infrared spectroscopy results have given insight into the molecular understanding for the significant role of the chloro groups in ZIF-71 on the adsorption of ethanol [121]. The potential for improved bio-ethanol recovery was highlighted as a result, as was the relevance for the design and development of new MOFs.

6.3. Other frameworks

A novel porous coordination polymer, copper [(tetrakis-*m*-pyridyloxymethylene)methane]Cl₂, or Cu(II)(mtpm)Cl₂ where mtpm is *tetrakis(m-pyridyloxymethylene)methane*, has been synthesized, and its adsorption isotherms for water, methanol, and ethanol found to be totally different from each other [122]. With methanol there is an adsorption induced lattice rearrangement, influenced by the extent of rearrangement of the framework and the affinity between host and guest. The MOF adsorbs water at low humidity and also methanol, but it does not adsorb ethanol. The material hence has the capacity to separate both methanol and water from bio-ethanol, which is a mixture of the three. A Monte Carlo simulation and free energy analysis of the adsorption-induced lattice transition observed in flexible frameworks of porous coordination polymers has demonstrated that the stabilization provided by the guest adsorption drives the structural transition [123].

6.4. Resistance of MOFs to water

Unfortunately, some MOFs such as MOF-5 are severely degraded by water. They were once considered relatively robust materials, with good stability in water vapour [124]. However, many other studies indicate that their adsorption properties deteriorate significantly upon exposure to water vapour [125–128]. The interaction of water with MOF-5 has been simulated by molecular dynamics, which suggest that MOF-5 is stable at low water concentrations, but unstable when exposed to ≥4% water [129]. This was explained by the weak interaction between Zn and O atoms, which allows for attack by the water molecules. An answer to the problem would be to design the Zn-carboxylate interactions such that they are stronger than the Zn-water interactions. Either electron withdrawing groups (halo or nitro) or electron donating groups (butyl or alkoxy) present in the terephthalate rings would be expected to have an influence on susceptibility to water attack, as will the nature of the metal centre. The dihydroxy version does not dissociate water until the temperature is between 150 and 200°C [130], and is claimed to be very stable overall [131].

Other important conclusions that have been reached [132] are:

- Metals with lower coordination numbers or higher oxidation states tend to be more stable towards water as they have greater metal-ligand bond strengths
- Zn-based MOFs were observed to be the most moisture sensitive because of their weak metal-oxygen coordination bonds.
- MOFs based on zirconium have been observed to be among the most stable, with exceptional hydrothermal stability.
- Higher basicity ligands result in greater metal-ligand bond strength, with MOFs based on imidazole [154] and pyrazole showing higher resistance to water than carboxylated MOFs.

Tetranuclear lanthanide clusters with organoboron-derived tricarboxylate ligands have been constructed that feature remarkable thermal and hydrolytic stability [133]. The influence of pH, particularly at highly acidic or basic values also needs to be known [134].

6.5. MOF Membrane performance

The highest fluxes for alcohols recovery were obtained for MOF-filled

silicone rubber mixed matrix membranes, and these had quite high separation factors (see Table 3). That for ZIF-8/PMPS in recovering *i*-butanol was 40, with a flux of 8.6 kg/m²h at 80°C [135]. ZIF-8 performs better than ZIF-7, profiting from the extra organophilic character provide by the 2-methyl substituent in the imidazolate ligand.

Table 3

Best performance data for ethanol and butanol recovery and organic separations by membranes based on metal-organic frameworks.

Feed, (wt%)	Membrane type	Sepn. factor	Flux, (kg/m ² h)	Temp. (°C)	Ref.
Ethanol					
5	ZIF-71 in PDMS	-	1.4	50	[97]
		-	0.8	50	
5	Al terephthalate/ PDMS	11	5.5	70	[102]
Butanol					
1	ZIF-7/PDMS	66	1.7	60	[107]
5		70	3.5	60	
<i>i</i> -, 1	ZIF-8/PMPS	35	6.4	80	[135]
<i>i</i> -, 3		40	8.6	80	
<i>n</i> -, 1	ZIF-8/PDMS	82	4.85	80	[110]
<i>i</i> -, 5	ZIF-71/PMPS	-	1.75	50	
Bio-, 1.2	Zn(TPA) ₂ (TED) _{0.5} / PEBA	17	0.63	40	[109]
Organic sepns.					
<i>n</i> -Hexane/ benzene	ZIF-8 on α -Al ₂ O ₃	23	0.43	20	[117]
Xylenes	MOF-5	-	(<i>p</i> -) 0.7 (<i>o</i> -, <i>m</i> -)	20	[101]
<i>m</i> -Xylene/ <i>p</i> -xylene	Zn ₂ (TPA) ₂ .DABC O	-		25	[105]
		1.6		150	
			(<i>m</i> -) 0.83 (<i>p</i> -) 0.41 (<i>m</i> -) 2.1 (<i>p</i> -) 0.53		

MOFs may also have potential in the separation of xylene isomers, as when at 150°C the respective *m*- and *p*- isomer fluxes are 2.1 and 0.53 kg/m²h [105].

7. Mixed matrix membranes

The properties and applications of polymer composites have been studied for many years, and are the topic of several text books [21,136]. There is a long history of the use of fillers to improve the separation characteristics of silicone rubber membranes [34,35,58,108,137–138]. The advantage of organic matrices and inorganic fillers is that they overcome the difficulties of manufacture of purely inorganic membranes.

Unlike dehydration applications with polar membranes, the matrix or host polymer in OPV is usually of a hydrophobic rubbery nature, as in PDMS and PTMSP, although glassy amorphous polymers like polyacetylene/poly(4-methyl-2-pentyne) or PAPMP have received attention. Somewhat surprisingly, the very hydrophilic poly(vinyl alcohol) or PVA has been used with an appropriate hydrophobic filler. Even cellulose acetate blends with PVA are effective in separating methanol/*tert*.butyl ether [139]. OPV results for composites based on all of these matrix polymers will be discussed according to the fillers employed.

For OPV applications involving organics removal generally, several kinds of inorganic fillers such as nanosilica [140], zeolites [141], carbon nanotubes [142], carbon molecular sieves [94,143] and polyphosphazene nanotubes [144] have been introduced into polymer casting solutions.

7.1. Silica/PDMS

Organophilic PDMS composite membranes containing silica nanoparticles have been made [140]. Both the flux and separation factor were increased by the presence of the silica, and the swelling of the membrane was

greater. For 5 wt.% ethanol/water at 70°C the flux was 0.21 kg/m²h and the separation factor 41.

An improvement in the ethanol selectivity of a silicalite membrane by incorporating a silicone rubber coating has been demonstrated [145,147]. Fluxes and separation factors were 0.22 kg/m²h and 120 for 5 wt.% ethanol/water at 40°C, and 0.42 kg/m²h and 100 at 60°C. These values were considerably higher than those obtained for the unfilled membrane, 0.06 kg/m²h and 14 respectively. A vinyltriethoxysilane-modified silicalite/PDMS hybrid has been prepared and a separation factor of ~30 obtained for 5.3 wt.% ethanol/water at 50°C [146]. The permeate pressure was 170 Pa.

A number of other researchers have prepared silicalite-filled PDMS membranes and obtained positive results, another example giving a flux of 0.15 kg/m²h and a separation factor of 34 for treatment of a 70 wt.% ethanol/water mixture at 22 °C [108,147]. A silicalite-filled PDMS/polysulphone composite membrane has flux of 0.23 kg/m²h and a separation factor of 7.5 for treatment of a 4.8 wt.% ethanol/water mixture at 60 °C, using a vacuum on the downstream side [30]. It has been found that it was not possible to separate mixtures of different alcohols with this system because of their small differences in solubility in the membrane, but ethanol could be separated from aqueous mixtures because of the low solubility of water in the membranes [147].

Capillary supported ultrathin (300 nm) silicalite/PDMS membranes have been tested for *iso*-butanol recovery [148]. They resulted in very high fluxes of up to 11.2 kg/m²h, with a separation factor of 32 for treatment of 3 wt.% *iso*-butanol at 80 °C. The potential of PV using silicone rubber-coated silicalite membranes for the selective separation of butanol from ABE solutions has been investigated [149]. The amount of compounds adsorbed from fermentations increased in the order ethanol < acetone < butanol. The flux of *n*-butanol reached 0.020 kg/m²h at 45°C, whereas that for ethanol and acetone was negligible.

Other improvements have been made by preparing different silicalite particles by hydrothermal synthesis in fluoride (F) or alkaline (OH) media, and then incorporating them into PDMS to prepare PDMS/silicalite membranes. Compared with silicalite (OH), the silicalite (F) particles had significantly fewer silanol groups and were more hydrophobic, thus showing higher selectivity to ethanol [150].

PDMS composite membranes containing industrial organophilic silica nanoparticles have been made, the composite being supported on a non-woven fabric substrate [140]. The flux and separation factor were increased by the presence of the silica, and the swelling of the membrane was greater. For 5 wt.% ethanol/water at 70°C the flux was 0.21 kg/m²h and the separation factor 41. These values were considerably higher than those obtained for the unfilled membrane, 0.06 kg/m²h and 14 respectively. A vinyltriethoxysilane-modified silicalite/PDMS hybrid has been prepared and a separation factor of ~30 obtained for 5.3 wt.% ethanol/water at 50°C [146]. The permeate pressure was 170 Pa.

7.2. Silica/PTMSP

Hydrophobic silica-filled PTMSP membranes in very thin layers on top of an ultrafiltration (UF) membrane have been applied to the recovery of ethanol [51,151]. Results were better than those obtained with a commercial membrane, Pervatech PDMS. With a support membrane of PVDF or PAN there was a more open hydrophobic structure, but the crucial factor was the thickness of the active membrane. The optimal membrane had a PVDF support and a 2.4 µm thick active layer, and gave a flux of 9.5 kg/m²h and a separation factor of 18. Unfortunately PTMSP ages physically or chemically so its performance deteriorates with time [48,51].

7.3. Alkoxysilanes/PVA

Membranes made from PVA crosslinked with 25 wt.% of tetraethoxysilane (TEOS) have been prepared for the OPV of aqueous ethanol, with the aim of minimising the swelling of the PVA [152]. Annealing of the membranes under nitrogen at temperatures of 100, 130 and 160°C was needed to complete the condensation reaction that introduced bridging, when higher permselectivity resulted. It was postulated that the crosslinking reaction took place in the non-crystalline parts of the PVA membrane, forming denser non-crystalline regions. Annealing also improved the selectivity of similar membranes made from poly(vinyl alcohol-*co*-acrylic acid) [153]. PVA has been crosslinked with γ -glycidoxypolytrimethoxysilane to produce PVA-silica hybrid membranes, with the aim of improving both permeability and selectivity [154]. The bridges formed have the structure:



The permeation flux for benzene from a mixture with cyclohexane increased from 20.3 g/m²h for an unfilled PVA membrane to 0.14 kg/m²h for the hybrid membrane, while the separation factor increased from 9.6 to 47. This was attributed to an increase in the size and number of both network pores and aggregate pores, and an elongation of the diffusion path.

7.4. Activated carbon/PDMS or PEBA

Early work on OPV experiments carried out with a toluene/ethanol mixture showed no improvement in selectivity and a decrease in flux for PDMS and various rubbery polymeric membranes filled with activated carbon [93,142]. With similar membranes made from the polyether block polyamide PEBA, trichloroethylene removal was enhanced [155].

Later work with carbon molecular sieves in PDMS membranes improved the OPV properties of the membrane for benzene removal from water [156].

7.5. Carbon nanotubes/PVA or PEBA

PVA membranes containing carbon nanotubes (CNTs) have been reported, with β -cyclo-dextrin being used as a dispersant [157]. They showed improved permeate flux and separation efficiency in OPV of benzene/cyclohexane mixtures, as well as better mechanical properties, compared with unfilled membranes. The work follows similar studies where graphite flakes or carbon molecular sieves were introduced into the membrane to give analogous improvements in both flux and selectivity [158]. The results were attributed to a higher free volume and more relaxed polymer chain packing which could reduce the mass transfer resistance and facilitate permeation of benzene. However, excessive filling inhibited permeation.

A composite membrane of CNTs in PEBA was tested in an OPV system incorporated with fermentation as an efficient way to relieve the feedback inhibition of butanol in ABE fermentation [159]. The addition of the CNTs to PEBA enhanced the removal flux of the solvents in a model solution test. The butanol flux at 37°C for a membrane with a 5 wt.% loading was 0.016 kg/m²h versus 0.010 kg/m²h for the unloaded PEBA, with the separation factors being 19 and 17 respectively. This removal rate resulted in a 61% increase in the batch with the CNT/PEBA membrane compared with that of the batch with PEBA alone. As well, the addition of the CNTs improved the mechanical strength of the membrane, leading to a longer operational time.

7.6. Zeolites/PDMS, PVA or PEBA

The incorporation of hydrophobic zeolites of the Y, ZSM-5 and ALPI-5 types into PDMS membranes significantly influences the OPV properties [141]. The selectivity for ethanol is increased as is the flux. The best result was a separation factor of 15 and a flux of 0.05 kg/m²h. In a more recent example the addition of 30 wt.% zeolite (TZP-9023) to a PDMS membrane after the addition of a crosslinker has led to a 10-20-fold increase in ethanol permeability for a 10 wt.% ethanol solution at 25°C [160].

A ZSM-5 zeolite/PDMS membrane with an 80% loading was investigated for butanol recovery from a 1.5 wt.% aqueous solution [161]. A vacuum was applied on the downstream side to give a <1 kPa driving force. The butanol flux was 0.13 kg/m²h compared to 0.10 kg/m²h for the zeolite-free membrane, and the separation factor was 33 versus 19. In a fed batch fermentation with incorporated OPV, ABE production from 172 g/L glucose had its overall butanol productivity and yield increased by 16 and 11% respectively. This was attributed to less butanol inhibition, to give a highly concentrated product containing 170 g/L of butanol which after phase separation gave a final product containing >600 g/L butanol.

The separation performance of multilayer PVA membranes filled with A-type zeolite strongly depends on the pore size of the zeolite [162]. Smaller pore sizes promote water selectivity but decrease its permeation, whereas the opposite occurs with a larger pore size zeolite. The alternative approach of totally filling the pores of a UF membrane with a suitable polymer has been much explored for aromatics/aliphatics separation [163].

Composite membranes have been made by incorporating ZSM-5 zeolite into PEBA membranes [164]. The membrane containing 5 wt.% of the zeolite showed preferential adsorption capacity for *n*-butanol, resulting in enhanced flux in its OPV recovery from aqueous solutions. The flux for a 4.5 wt.% solution at 35°C was 0.95 kg/m²h for a membrane with a 10 wt.% loading of the zeolite, versus 0.55 kg/m²h for the unloaded membrane. The separation factor was little changed at 24 and 27 respectively. When the zeolite content

reached 10 wt.% it was found that agglomeration of zeolite in the membranes occurred, and there was an increased transport resistance. As the feed temperature and concentration were raised the organic flux increased more than that of water and a higher selectivity resulted.

7.7. Summary of results for mixed matrix membranes

For mixed matrix membranes the main applications where they could be of benefit are in the separation of organic compounds, but the flux rates are extremely low, as shown for the selection in Tables 4 and 5. A very thin layer of PDMS around silicalite gave the best flux, that for *i*-butanol being 11.2 kg/m²h [148], whereas a styrene/SBR membrane was the best performer for benzene/cyclohexane separation [57].

Table 4

Best performance data for ethanol and butanol recovery from aqueous solutions using silica-based mixed matrix membranes.

Feed, (wt.%)	Membrane type	Sepr. factor	Flux, (kg/m ² h)	Temp. (°C)	Reference
Ethanol					
5	Silica/PDMS	41	0.21	70	[140]
70	Silica/PDMS	34	0.15	22	[145]
5	Silicalite/PDMS	120	0.22	40	[145]
		100	0.42	60	
70	Silicalite/PDMS-polysulphone	7.5	0.23	60	[30]
Butanol					
<i>i</i> -, 3	Silicalite/300 nm PDMS	32	11.2	80	[148]

8. Recoveries from fermentation liquors

8.1. Batch processes

Ethanol removal from a 5-10 wt.% ethanol/water solution has been demonstrated with an ethanol-permeable membrane based on PDMS, which produced a 30-40 wt.% ethanol enriched permeate [7,90,165]. This was followed by an innovative condensation technology ("dephlegmation"), consisting of a partial condensation with counter-current flow of rising vapour and falling condensate. With a dephlegmator, better separation can be achieved and only vapour condensing at the top of the column needs to be cooled to the lowest temperature. A second dehydration step, PV with a more water permeable membrane, is used to treat the ethanol obtained from the dephlegmator. In this step, the last 10 wt.% of water in the alcohol vapour is removed to produce a 99.5 wt.% dry alcohol. A mathematical model of the system has indicated that it is more efficient than distillation, and leads to an improved separation performance [166]. The combination process is claimed to be cost-effective and energy efficient in recovering ethanol from biomass, and may offer the possibility of small-scale production of bio-ethanol in rural areas.

Table 5

Non-aqueous organic separations explored with various mixed matrix membranes.

Organic compound	Membrane type	Temp. (°C)	Sepr. Factor	Flux (kg/m ² h)	Reference
Toluene/ethanol	Carbon/EPDM	20	-	0.03	[142]
	Unfilled EPDM		-	0.06	
	Carbon/PDMS		-	0.06	[158]
	Unfilled PDMS		-	0.80	
Benzene/cyclohexane	Alkoxysilane/PV A	50	47	0.14	[158]
	Unfilled PVA		9.6	0.02	
	CNTs/PVA	50	-	0.05	[157]
	Unfilled PVA		-	0.02	
	Styrene/SBR	20	5	1.04	[57]

Table 6
Best performance data for ethanol and butanol recovery using various membranes.

Feed, (wt.%)	Membrane type	Sepn. factor	Flux, (kg/m ² h)	Temp. (°C)	Reference
Ethanol					
4.3	PDMS 5-10 μm layer/ceramic support	6	20	70	[24]
		6	5.2	40	
5	Silicalite on steel support	30	4.0	60	[87]
10	NaA zeolite	-	2.2	75	[76]
			4.5	105	
Butanol					
<i>n</i> -, 5	PTMSP ^a on PTFE/silica	104	9.5	50	[51]
10	Silicalite on Al ₂ O ₃	10	4.0	60	[78]
<i>i</i> -, 3	ZIF-8/PMPS	40	8.6	80	[135]
<i>i</i> -, 3	Silicalite/300 nm PDMS	32	11.2	80	[148]

^aPoly(trimethylsilyl-1-propyne)

8.2. Continuous fermentation

The main obstacles to feasible industrial scale use are low yield and high separation costs [167]. There is a vast literature on the use of OPV in the continuous operation of fermentation processes for bio-fuel production [5,7,11,40,168–174]. Its main aim is to remove bio-alcohols before their cell toxicity level is reached and so ensure satisfactory continuous operation. Reviews include economic assessments of the different fermentation methods [170]. PDMS membranes have usually been employed, but fluxes were generally quite low, at up to 0.07 kg/m² for ABE recovery by OPV [174], except for one result for ethanol of 3.3 kg/m²h using a silicalite/PDMS composite membrane [41]. A more recent example had fluxes ranging from 0.34 to 0.85 kg/m²h and separation factors for butanol ranging from 5.1 to 27.1, using a PDMS/ceramic composite membrane [175]. Membrane fouling has been highlighted as another problem [176,177], with the flux and selectivity decreasing in an ABE fermentation broth compared to an inactive fermentation broth [178]. The membrane was fouled by microbial cells and the components of disrupted cells in the integrated process. Performance was partially recovered by a water rinse of the membrane, and other measures such as a UF pretreatment have been found to be useful, although these add to the complexity of the system. Productivity was 38% greater than that of the batch mode. Employing a silicalite/PDMS-PAN composite membrane for solvent recovery has yielded a separation factor >30 and a total flux of 0.49–0.71 kg/m²h, with membrane fouling being negligible with an occasional water wash of the membrane [178].

The potential advantages outlined by these workers and others [4,27] include:

- Control of product inhibition
- Cell retention
- Less stress for cells
- Potential for high enrichment of product
- Simpler product purification
- Cost effective
- Better conversion yields in shorter times
- Positive environmental aspects
- The non-porous membrane structure precludes fouling by microorganisms or colloids
- Teat from exothermic bioreactions can be released into the OPV unit
- There is an absence of thermal, chemical or mechanical stress on the fermentation broth

9. Comparison of membrane systems

A summary of results for the best performing membranes is shown in Table 6.

10. Conclusions

For ethanol recovery, flux rates are highest for a non-polar organic polymer such as PDMS when used as a very thin PDMS layer on a supporting

base. Of the inorganic membranes NaA zeolite gives the highest separation factors and also reasonable fluxes. Hydrophobic silicalite also performs well.

For butanol recovery, flux rates are best for silicone rubber mixed matrix membranes containing silicalite or ZIF nanoparticles, with ZIF-8 or zinc(2-methylimidazole)₂ the best so far. MOFs need to be designed with ligands that give rise to an adequate pore size and result in a hydrophobic membrane, and must be stable in an aqueous environment.

Examples of the separation of organic compounds show that MOFs dominate the scene here also, with good fluxes for *n*-hexane/benzene separation, and to a lesser extent for the separation of xylene isomers at high temperature. In this area pore geometry becomes important. A styrene/SBR membrane gives a reasonable result for benzene/cyclohexane.

Apart from the usefulness of OPV in the recovery of alcohols from batch fermentations, of more import is the prospect of their direct removal from fermenters to ensure that the cell toxicity level of the alcohol is not reached and continuous operation is feasible.

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